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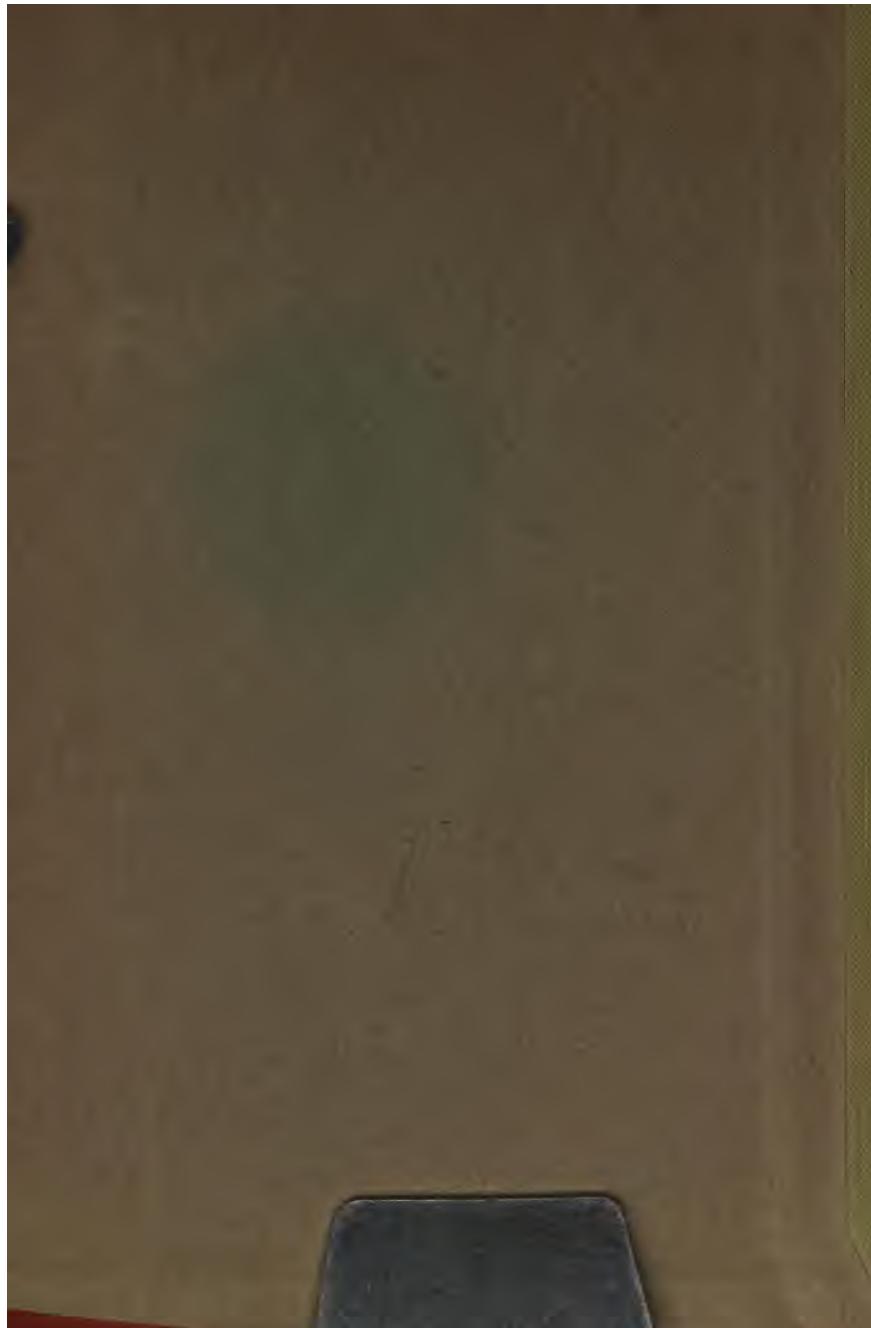
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**COLLOIDAL AND CRYSTALLOIDAL
STATE OF MATTER**

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THE COLLOIDAL AND CRYSTALLOIDAL STATE OF MATTER

BY

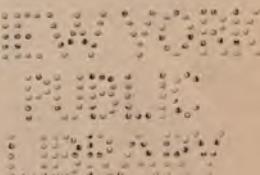
Dr. PAUL ROHLAND

A.O. PROFESSOR AT THE TECHNISCHE HOCHSCHULE, STUTTGART

Translated by W. J. BRITLAND and H. E. POTTS, M.Sc.

She is the unique artificer, from the simplest substances to the greatest contrasts, without appearance of exertion to the greatest perfection; to the most accurate precision, ever suffused with somewhat of delicacy.

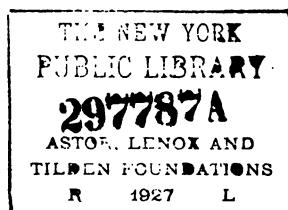
—GOETHE ("Nature")



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P R E F A C E

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IN the last decade the colloidal state of matter, or, in other words, substances in the colloidal state, (in contradistinction to those in the amorphous or crystalloidal) have come to the front technically and scientifically.

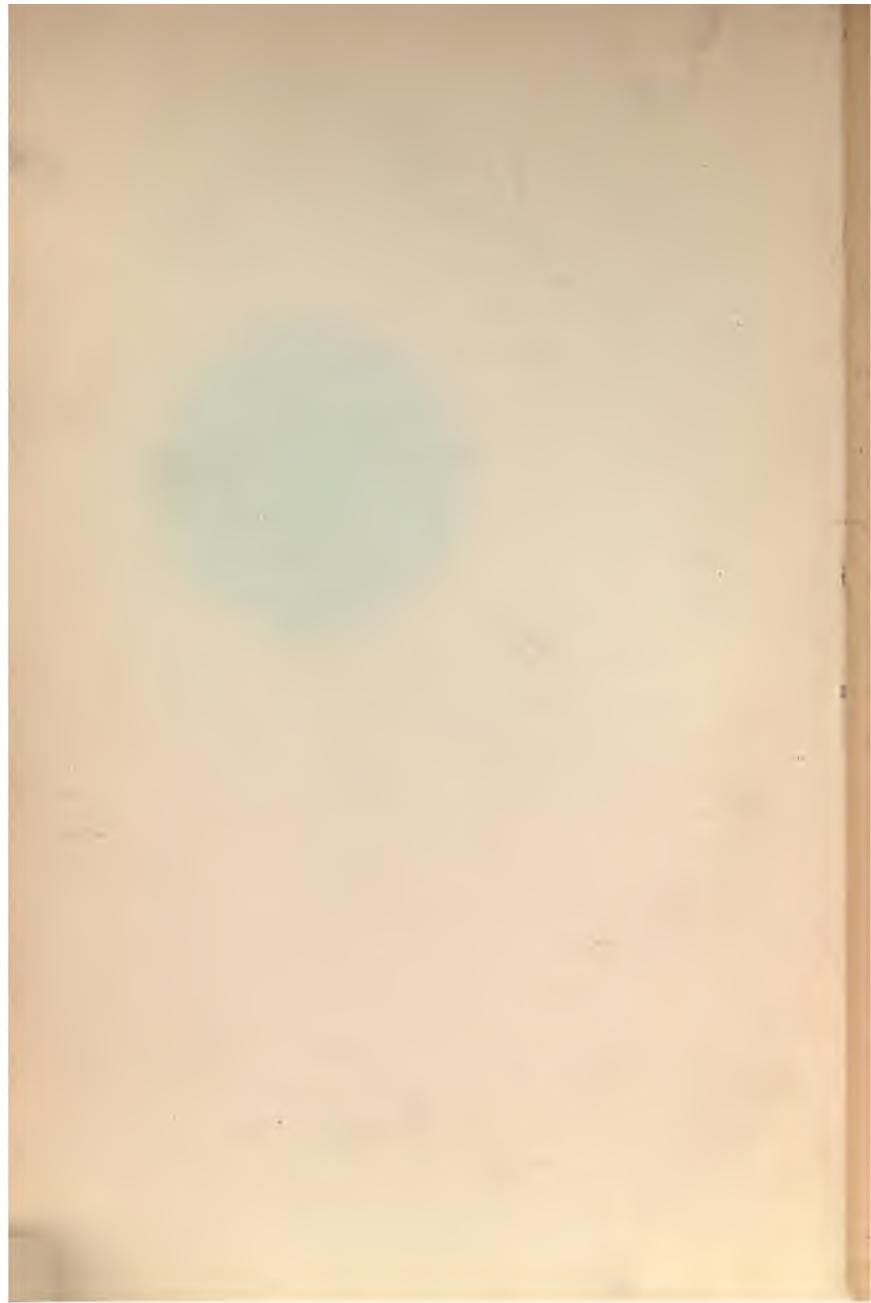
This region of work covers a very wide field, inorganic and organic chemistry, physics and physiology ; in all these branches knowledge of this kind has proved fruitful, and will do so still more.

But the scope of this field must be extended still further ; technology and agriculture, mineralogy and geology feel its effects ; and since spontaneous generation must presumably be sought in the colloidal state, modern natural philosophy cannot pass over this line of division between the monistic and dualistic conceptions of the universe without taking up a firm position here.

So this subject concerns everyone who is not opposed to, or ignorant of, modern natural science, whether he is a technologist, industrialist, chemist, physicist, forestry worker, practical doctor, physiologist or natural philosopher ; it will lead to work yielding splendid fruit, and perhaps to the latent secrets of nature still to be disclosed. This pamphlet is written for general orientation in this field.

PAUL ROHLAND.

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THE COLLOIDAL AND CRYSTAL- LOIDAL STATE OF MATTER

THE significance in nature, as in technology and History of agriculture, of colloidal substances, or better, Colloids. substances in the colloidal state, has first been made clear during the last ten years.

Substances in the colloidal state were certainly employed in the earlier stages of human culture, *e.g.*, as adhesives; it is now known that the old Egyptians used substances such as starch and dextrin in the dyeing of materials, and the Chinese allowed their clays and porcelains to decompose, to increase the colloidal substances in them and to raise the degree of plasticity.

But till the time mentioned the interest of scientists was essentially confined to the substances which attracted attention by their colourless or splendidly coloured crystal forms, and by their energy of crystallisation were easily susceptible to research.

In this connection it must be remembered that since Lavoisier and the commencement of scientific chemistry more than a century ago, much greater difficulties have arisen and still remain in the investigation of substances in the colloidal state than in crystalloidal bodies.

And yet it must be recognised that matter in the colloidal state plays a much greater part in nature, and logically also in technology, than has hitherto been ascribed to it.

In Germany, during the peaceful years of the sixties of the last century, the single branches of the so-called mental sciences were pursued to full development; in

England, on the contrary, the natural sciences triumphed.

In 1859 Darwin published his fundamental work on the Origin of Species; in 1856 Perkin prepared the first aniline dye from tar, mauveine, a beautifully coloured substance in the crystalloidal state.

At that time men began to occupy themselves scientifically with substances in the colloidal state.

Thomas Graham, in the years 1861 to 1864, was the discoverer of the characteristic properties of substances in the colloidal state in silicic acid, an inorganic colloid; he added hydrochloric acid to a solution of sodium silicate contained in a dialyser (a vessel enclosed by vegetable parchment paper), and observed that the crystalloidal salt, formed by the decomposition of these substances, diffused through the membrane into the vessel beneath filled with pure water, but the silicic acid, separated in the colloidal state, did not possess this property. The process of dialysis was discovered.¹

With the assistance of an idea borrowed from mechanics an explanation is easily found for this phenomenon; in the light of the molecular, and further of the ionic hypothesis, it is easy for the molecules and ions of the sodium chloride to diffuse through the membrane, while the larger colloidal molecules of the silicic acid are held back.

Graham² quite correctly distinguished between the **crystalloidal** and **colloidal state** of matter; it was later in chemical text-books and handbooks that this conception suffered displacement, in that the line of distinction was drawn between **crystalloidal** and **colloidal substances**.

List of
Colloids.

This classification must now be considered invalid, since for each substance both the crystalloidal and colloidal state is assumed. A very large number of

¹ Dialysis was already known two years earlier, but not in this definite scientific manner.

² Liebig's Ann. 121, 1, 1862.

inorganic bodies, which were hitherto known only in the crystalloidal state, have already been prepared in the colloidal, *e.g.*, almost all metals and metalloids; of the latter, perhaps only red phosphorus and iodine are lacking.

To these must be added their simplest compounds, the oxides, sulphides, and chlorides. Also different carbonates, chromates, phosphates and sulphates have been obtained in the colloidal state; further, dyes, such as indigo and benzopurpurin, and organic substances, such as caramel and glycogen. All these bodies are known both in the crystalloidal and colloidal state.

Even substances which were hitherto assumed to possess a marked crystalloidal character, as heavy spar, barium carbonate,¹ gypsum,² common salt and sylvine, can be transformed into the colloidal state.

Further, gelatinous gypsum is obtained by the addition of alcohol to natural or artificial sea-water; zoologists may decide whether this colloidal gypsum is identical, as Möbius has observed, with the *Bathybius Haeckelii* (E. Haeckel, "Natural History of Creation"), the primitive slime-life of the greatest sea-depths, which inhabits these depths in the form of naked clumps of protoplasm and slime-nets.

Another series of substances is as yet known almost wholly in the colloidal state; the most important organic substances, such as the proteins, belong to this class.

Inorganic substances of this kind are the hydroxides of many metals and metalloids, also dyes, such as molybdenum blue, purple of Cassius, Prussian blue and copper ferrocyanide.

The most important organic substances in the colloidal state are starch, dextrin, inulin, tragacanth, tannin, the latex of *Castilla plastica*, catechu, gum, rubber, sumach; also, of great importance, glue and

¹ Zt. f. Chem. u. Ind. der Koll. 1, 166, 1906.

² P. Rohland, Zt. für Anorganische Chemie, 65, 206, 1910. (The Hydrosulphates and Sulphates of Barium and Calcium.)

gelatine, derived from mammals (gluten), from fishes (*Ichthycolla*, isinglass), and from plants (agar-agar); caseins and albumins (ovalbumin, serumalbumin, haemoglobin); finally, invertin, emulsin, trypsin (enzymes), bacteria-jellies, and cell-protoplasm belong to this class.

Chrono-
logical
Order.

Concerning the chronological order in which different substances have been obtained in these states, the substances of more simple structure, such as common salt, gypsum, lead chloride, were first known in the crystalloidal state, and have been prepared in the colloidal state more recently. Exactly the reverse holds for the substances of more complicated structure, such as starch, gelatine, albumin, etc.

These were first known in the colloidal state, and only quite recently have they been obtained crystalline, *e.g.*, white of egg. Also in the protein of the turkey-hen's egg an albumin has been found which is crystalline, and which answers to the formula $C_{258}H_{422}N_{63}O_{88}S_3$, and is probably isomeric with the crystalline egg albumin.¹

It is now fairly certain that the transformation of probably almost all substances from the crystalloidal to the colloidal state can be effected, yet the reverse problem, the preparation in the crystalloidal state of substances previously only known in the colloidal, has been hitherto little attacked.

A very large part of the class of substances here named colloids occurs in nature; in the inorganic kingdom, at all events at the present time, the crystalloid form preponderates; in an earlier epoch colloidal forms very probably predominated. In the organic kingdom will be found the chief representatives of substances in the colloidal state, the starch and albumins of plants.

Formation
of Colloids
in Nature.

The sun throws down heat on the green-foliaged roof of the beech-wood; the air shimmers and glitters almost in silence between the branches; only the

¹ Journ Russ. Phys. Chem. Ges. 38, 597, 1906.

whirling flight of insects vibrates through the heated atmosphere. Behind this network of wood a great and mysterious process is being consummated. The green leaves of the beeches do not lie in dreaming rest, mysterious forces are borne to them in the quivering sunlight; a stream of air which carries carbonic acid gas rustles steadily across them and into them by their decomposing action.

In the leaves occurs the decomposition of carbon-dioxide into its component substances carbon and oxygen; the two elements are torn apart by the transversally oscillatory ether waves and the chlorophyll particles in the single cells of the leaves themselves. A wonderful manufactory is established in the leaves, which in a way yet unknown conducts this separation by means of radiant energy and chlorophyll, returns the free oxygen to the air, and works up the carbon to substances in the colloidal state, especially to starch.

Now the heat of combustion of starch to carbon-dioxide and water amounts to 4,123 calories per gramme; therefore, according to the first law of Thermodynamics, the same amount of energy is necessary to form starch from carbon-dioxide and water. Since the reduction of carbonic acid gas only occurs in sunlight, this radiant energy is furnished by the sun.

Will man succeed some day in imitating this process, in discovering these wonderful energies, partly electronic and partly chemical, and in utilising them for his own purposes? Who can say to-day?

These processes in the green leaves consist of several stages; in one the carbon-dioxide is reduced to carbon; in another carbon and water combine to form carbohydrates, starch, etc., with simultaneous evolution of oxygen; and in a third these combine, probably in the sieve-tubes, with oxygen and nitrogen compounds already formed or taken up from outside, together with sulphur and phosphorus compounds, in a many-kinded synthesis to a further substance in the colloidal state, plant protein. From there

outwards the protein wanders into the animal kingdom into animal bodies, in which are contained substances in the colloidal state constituted in the most varied forms, such as albumin, casein, etc.

Distinctions between Colloids and Crystalloids.

Diffusion.

Osmotic Pressure.

Freezing-point and Boiling-point.

Molecular Weight.

Beyond their behaviour in the dialyser, substances in the colloidal state exhibit the following distinctions from crystalloids; these differences occur especially in solution.

Dissolved colloids possess a much smaller energy of diffusion than crystalloids; their velocity of diffusion into other liquids is much less than that of crystalloids; thus, according to Graham, the diffusion of crystalloidal sodium chloride is 2·33, while that of colloidal protein is 49.

In consequence of their lack of capacity to diffuse through vegetable or animal membranes, dissolved colloids possess a much smaller osmotic pressure than crystalloids; according to Pfeffer the osmotic pressure of a 1 per cent. solution of sugar is 51·8 cm. mercury, while that of a 1 per cent. gum solution is only 6·9 cm. mercury, a 1 per cent. dextrose solution only 16·6 cm. mercury.

Further, while with crystalloidal substances the freezing-point falls proportionately to the quantity added, with dissociated substances about double the amount, this lowering of freezing-point is quite minimal for substances in the colloidal state; e.g., 44 gms. of protein dissolved in 100 gms. of water caused a lowering of the freezing-point of only 0·060°.¹ The same holds for the raising of the boiling-point. Colloidal solutions, e.g., very concentrated soap solutions, have the same boiling-point as pure water; with crystalloidal dissolved substances the boiling-point rises proportionately to the quantity added. Further, colloidal solutions cannot be distilled without decomposition.

To explain this behaviour an enormously greater molecule, and a correspondingly great molecular weight, has been assumed for substances in the colloidal state;

¹ Zt. f. Phys. Chem. 9, 88 (1892).

for silicic acid about 50,000, for starch about 25,000, while this figure for a crystalloidal substance like sodium chloride is 58·5. From the relatively simpler constituted molecule of tungstic acid to albumin there is an increasing complication in molecular structure; the molecular weights themselves, as far as present measurements go, are assumed to increase from 1,000 to 50,000.

Corresponding to the simple functions exerted in the economy of nature by common salt, for example, its molecule is simply constituted, its molecular weight relatively low; the state in which it almost always occurs is the crystalloidal, its crystalline form is the simplest possible, the regular.

It has been prepared recently for the first time in the colloidal state,¹ though it may be noted that it frequently exists in the animal organism in this state.

Corresponding to the complicated functions possessed by substances such as glycogen, casein, albumin, their molecules are constituted in the most varied and complicated manner, their molecular weights are so high that they can only approximately be estimated, the state in which they occur is the colloidal, very rarely the crystalloidal.

There is, however, the possibility that simply constituted substances such as common salt, lead chloride, mercurous chloride, gypsum, which in the crystalloidal form possess a small molecular weight, may possess in the colloidal form a large molecular weight, such as has already been assumed for silicic acid, ferric hydroxide, etc.

An interesting insight might be thus obtained into the constitution of these substances, which in this form is perhaps more complicated than has been hitherto assumed.

Further, colloids are characterised by their capacity for scattering and polarising a beam of light, e.g., optical behaviour.

¹ Berichte. d. Deutsch. Chem. Ges. 38, 597, 1906. C. Paal (Colloidal sodium chloride).

colloidal gold and silver can thus be resolved into finest suspensions in the ultra-microscope, with which 0·000004 mm. can be still seen.

Crystallisation in crystalloids answers in colloids to a process which is designated coagulation.

Compared with the complicated process of crystallisation, this coagulation is perhaps the simpler, yet it was investigated much later.

**Coagula-
tion and
Crysta-
llisation,**

The differences between the processes are considerable; crystallisation can proceed slowly, *e.g.*, in a moderately concentrated solution; it can, indeed, in rare cases be brought about suddenly, *e.g.*, in supersaturated solutions of Glauber's salt or supercooled water.

The process of coagulation always occurs in the latter way. Crystallisation and coagulation can both be brought about by change in temperature, but coagulation can also be effected by addition of electrolytes; only in the case of a supersaturated crystalloidal solution, or of supercooled water, can sudden crystallisation be caused by addition of a crystal.

The following coagulate, or change from the state of sol to that of gel:—metal and metal sulphide hydrosols on addition of an electrolyte; glue (*colla*), gelatine, by lowering of temperature; casein and albumin by rise of temperature, both also on addition of electrolytes, such as calcium chloride and calcium sulphate; other albuminates when what we call "life" vanishes from the tissue. In crystalloidal solutions this is not the case; the first process shows the intimate relationships existing between matter in the colloidal state and the phenomenon of life. If the gel¹ can be transformed into the sol¹ again by the addition of water, the process is reversible; in the opposite case the change of state is irreversible; fish-glue is a type of the reversible colloid, silicic acid of the irreversible.

A further property of colloidal solutions is that of passing through a filter. Colloidal solutions will be

¹ [These words are transposed in the original, obviously by mistake.—Tr.]

considered as very finely divided suspensions or emulsions.

The colloidal state of matter also possesses relationship with electrical energy. Colloidal solutions show a decrease of electrical conductivity, and, correspondingly, a much smaller reaction capacity than crystalloids. Thus the conductivity of colloidal ferric hydroxide decreases as the content in colloidal particles increases; when the latter is increased one hundred times, the conductivity is decreased by 25 per cent.¹ The conductivity of solutions of the alkali silicates is much smaller in comparison with that of the hydroxides, on account of the silicic acid hydrolytically separated in the colloidal state.² Further, if an electric current is passed through a colloidal solution, the particles of arsenic sulphide, clay, charcoal, tannin, gelatine, gum, glycogen, protein, starch, wander in the direction of the negative current; others, such as ferric hydroxide and aluminium hydroxide, in that of the positive.

In connection with this stands the theory of coagulation based on the fundamental electrostatic laws.³ According to it, coagulation occurs when the ions, added or already present, attract to themselves the particles in the colloidal state carrying opposite electric charge; they form complexes with them which gradually sink to the bottom.

But when ions and colloidal particles of the same charge meet, according to the fundamental electrostatic laws, a repulsion of the particles occurs, so that the colloidal state is maintained.⁴

With this is connected also the following phenomenon: Suspensions of very finely divided crystalloidal substances, such as calcium carbonate, calcium

Colloidally Composed Substances.

¹ Compt. rend. 143, 46—49, 1906.

² Journ. Phys. Chem. 2, 17, 1888.

³ Zt. f. Phys. Chem. 45 (1903), 51 (1905).

⁴ Regarding the "Theory of Colloids," I would refer to the "Grundriss der Kolloidchemie" of Dr. Wo. Ostwald. Publisher: Th. Steinkopff, Dresden.

sulphate, barium sulphate only remain suspended in water for a short time, perhaps an hour; also the addition of electrolytes is without any action on them; the particles remain suspended and do not sink to the bottom.

On the contrary, suspensions of colloidally composed substances, such as talc, clay, ultramarine, cement, remain suspended days, and indeed weeks; these substances in contact with water form bodies in the colloidal state, the hydroxides of silicon, aluminium and iron; the more colloidal bodies a substance can form the more markedly occurs the phenomenon of long continued suspension. Further, such suspensions sedimentate rapidly by addition of electrolytes; salts, such as common salt, sodium sulphate, calcium sulphate, accelerate sedimentation. Thus a suspension of ultramarine, which remains suspended ordinarily for about ten hours, is sedimentated by addition of sodium chloride in twenty-five minutes, and by sodium nitrate in ten minutes.

There are two causes for this behaviour: the electrostatic attraction between the particles of suspended substances, which are surrounded by a colloidal envelope causing suspension, and the ions carrying the opposite electric charge; and, moreover, the removal of the water of the colloid; those substances in particular, such as calcium chloride, aluminium chloride, and ferric chloride, which possess hygroscopic properties, have the most powerful action, in that they attract to themselves the water of the colloid, which may amount to 5--10 per cent., when the destruction of the colloidal envelope and the sedimentation of the suspended substance follows.¹

Permeability.

There is another law which must be formulated otherwise, and cannot serve as a principle of distinction between substances in the colloidal and crystalloidal state.

¹ Cf. P. Rohland, Phys. Chem. Zentralblatt, VI. 1908, on the behaviour of suspended substances in the crystalloidal and colloidal state.

It has been said hitherto that a gelatinised colloid can no longer be taken up by a second colloid, whose diffusion it hinders while it allows dissolved crystalloids to pass through. However, in the dialysis of sodium silicate Graham represented a sharply defined case; in most cases the capacity of diffusion of colloidal solutions cannot be neglected, and in dissolved crystalloids the velocity of penetration shows great differences.

Thus coagulated silicic acid is impermeable to magnesium salts, or their velocity of diffusion is at all events very small.

It appears that the magnitude of the velocity of diffusion changes considerably, on the one hand, with the nature of the coagulated colloid or of the membrane used, and on the other hand with the nature of the crystalloidal solution.

Many substances in the coagulated state readily permit the diffusion of the crystalloid water, but not of substances dissolved in it which have also a crystalloidal nature, at least only to a small extent.

Copper ferrocyanide is permeable to water, but not to sugar, saltpetre, hydrochloric acid and many dyes which dissolve in it.

Plant and animal membranes also allow water to pass through, but permit the passage of substances soluble in it only slowly if at all.

Further, the envelope of the cell protoplasm is permeable to water, but not to many substances present in the cell juices, e.g., glucose, potassium and calcium malates, and some inorganic salts.¹

According to von Calcar, the permeability of the prepared amniotic membrane of the human embryo varies with the tension; by this membrane two elements of the diphtheria toxin, the toxins and the toxones, can be separated.²

On the contrary, the behaviour of rubber with water is exactly the reverse; in this case it is not permeable, though it is for many organic liquids.

¹ Zt. f. Phys. Chem. 2, 215, 1888.

² Zt. f. Chem. u. Ind. der Koll. 1, 5 (1906).

Probably the degree of permeability depends on the condition of the net structure of the coagulated substances.

Toxicity. Further, the poisonous action of barium salts in the colloidal state is smaller than in the crystalloidal.

It is probable also that in the remedy given by Bunsen for arsenic poisoning, ferric hydroxide, its colloidal state is of essential significance in this protective action; it would be of physiological interest to test whether colloidal aluminium hydroxide shows an analogous behaviour. The same holds for magnesium hydroxide (Antidote).

Water of Gelatinisation. Water of gelatinisation is particularly characteristic of the colloidal state; this takes the place of water of crystallisation in substances in the crystalloidal state.

Chevreul was the first to distinguish water of gelatinisation as bound by capillary affinity; he understood by this an attractive force of both physical and chemical nature.

Graham interpreted this definition in the following manner: That chemical affinity of the lowest degree can grade into capillary attraction, though the content in water of gelatinisation is still to a certain extent "truly chemical" as the content in water of crystallisation is, but that the combination of a colloidal substance with water is, however, only weak.

The transformation of colloidal water to the crystallised state can only be effected with difficulty; the compound of a substance in the colloidal state with water is, however, of a different nature than of a substance in the crystalloidal state. Different degrees of strength in the binding or linking of the water of gelatinisation to colloidal substances have been observed; the water is the more firmly bound the less it is adsorbed.

Little success has hitherto been attained in transforming substances from the colloidal to the crystalloidal state under artificial conditions; silicon hydroxide and aluminium hydroxide can be obtained in a crystallised state from their colloidal solutions;

however, months and years, together with periodic changes of temperature, are required for this purpose. According to a supposition by W. Ostwald¹ smoky quartz has resulted in this way in nature.

The colloidal state shows some other phenomena worthy Viscosity. of note; the viscosity is diminished by the presence of certain kinds of ions; e.g., in different organic substances and in clays, hydroxyl ions of definite concentration bring about this diminution.² In these cases this is to be ascribed to mutual repulsion of the negative hydroxyl ions, and the similarly negatively charged colloidal particles of clay.

Further, in reactions between substances in the colloidal and crystalloidal state, no compounds appear in rigid stoichiometrical proportions; adsorption compounds are formed which do not give the customary reactions; these first reappear when the colloidal system is destroyed.

Adsorbed permanganate does not react with hydrogen peroxide, sulphurous acid, ammonium sulphide; adsorbed ferric chloride does not give the Prussian blue reaction.

$\text{CO}_3^{''}$ and HCO_3' ions adsorbed by cement cannot be detected with twice-normal hydrochloric acid;³ vigorous evolution of carbon-dioxide with copious formation of ferric chloride first occurs on addition of concentrated hydrochloric acid; the adsorption system is first destroyed by this, whereby the appearance of the ordinary reaction is secured.

With the binding of these ions and their apparent disappearance in colloidal structures is connected a certain slowness or incapacity of reaction, such as in the slightly dissociated mercury cyanide.

The following are two analogous phenomena in which the solubility of the adsorbed substance is changed or reduced to zero; bottle glass often contains sodium

Adsorp-
tion and
Failure to
React.

¹ "Outlines of inorganic chemistry."

² Cf. P. Rohland, "Die Tone." A. Hartleben, Vienna, 1909.

³ P. Rohland (The slowness of reaction of adsorbed $\text{CO}_3^{''}$ ions).

sulphate in large quantities, which has not been reduced to sulphurous acid by the coal in manufacture. It is now impossible to remove this from the manufactured glass by lixiviation with water: the adsorbed sodium sulphate has become insoluble in water.

Only when the glass is broken up and digested with water for a long time in the pulverised state does the sodium sulphate contained in it pass into solution.¹

In the burning of bricks, especially with easily sintering raw material, an adsorption compound is formed between the silicates and the sodium sulphate, magnesium sulphate, or calcium sulphate, whose tendency to dissolve in water is likewise zero; water which accidentally comes into contact with the bricks does not dissolve these salts; even when, in consequence of the porosity of the bricks, the water penetrates to the interior, these sulphates are not dissolved out. This is very important in considering the technology of building.

It has been established that a fairly high temperature is necessary to form this adsorption compound between the sulphate and the aluminium silicate; on gentle ignition these salts are not adsorbed, though this is the case on moderate and vigorous ignition at about 1050—1090°. Moreover, it also depends on the condition of the raw material, whether or not such a compound between the silicates and sulphates is formed.

The content in adsorbed salts only amounts to 0·03—0·04 per cent., yet if they are not adsorbed in the process of burning they are later the cause of decomposition and decay, which give rise to injury and destruction of the surface of the brick.

Adhesion. The colloidal state of matter also shows two very characteristic physical phenomena. The single particles have a most marked tendency not only to cleave firmly to one another, but also to foreign bodies, a property which is very advantageous in concrete and ferro-concrete.

Formation of Foam. The other physical phenomena, foam formation, can be observed above all when substances in colloidal

¹ P. Rohland (Two processes in pot and glass manufacture). Zt. f. Angewandte Chemie, 20, 44, 1907.

solution, together with free alkali or free acid, are mechanically agitated; in organic colloids, in the most marked way in soaps, and further in protein; in inorganic colloids in the talcs, when they form silicon hydroxide in contact with water and dilute hydrochloric acid.

* * * * *

A detailed representation of the extremely weighty Colloids, position which substances in the colloidal state assume Tech-
nology and in almost all branches of technology and numerous industries would exceed the scope of this work. Some important Industry.
industries may be mentioned here, for which matter in the colloidal state has become of great importance.

This has come about in connection with an industry which at the first glance appears very remote—that of cement and clay.¹

The constitution of cement and the cause of its Cement
hardening have been fruitlessly investigated for ten Manufac-
years. The problem of hardening reflects in its develop-
ment all phases of the development of chemical theory.

Formation of silicates, their decomposition in different ways, arrangement of the atoms in the sense of the organic structural theory, were given successively as the cause of hardening.

The problem of hardening has been first pursued more searchingly on the basis of a knowledge of the properties of substances in the colloidal state, and the impenetrable veil which surrounded it has been, for the most part, removed.

From the adsorption compound, into which the calcium oxide has entered during the process of burning and sintering of the cement, the hydroxides of silicon, aluminium, and iron split off in the colloidal state on mixing with water, and are slowly coagulated by the calcium oxide, simultaneously partially hydrolytically separated and hydrated.

Further, these colloidal substances which are formed completely adsorb carbon-dioxide from the air, and from

¹ Cf. P. Rohland, Zeitschrift für Chemie und Industrie der Kolloide, IV. 5, 1909. Publisher : Th. Steinkopff, Dresden.

this adsorption the formation of calcium carbonate from the calcium hydroxide follows.

The substances coagulated by swelling now act like glue or paste, and hinder a further permeation into the interior of the hardening cement, and the further process of hydrolysis. Moreover, the gradual coagulation causes the hydration to occur, not suddenly as in ordinary quicklime, but very slowly. Accordingly the "constitution" of hardened cement is as follows:—it consists essentially, both on the surface and in the layers beneath, of calcium carbonate which results from the hydrolytically separated lime and the carbon-dioxide, and, further, of the coagulated hydroxides of silicon, aluminium and iron.

Concrete
and Ferro-
concrete.

The substances in the colloidal state formed by cement on mixing with water are connected also with its application in combination with gravel, broken stones, and rubble as concrete and ferro-concrete.¹ The colloidally deposited hydroxides of silicon, aluminium, and iron have the capacity of taking up amorphous or crystalloidal bodies, and surrounding them solidly; after the coagulation of cement with gravel, etc., this combination forms an extremely resistant mass.

The strong adhesion of concrete to cement, which amounts to 40—47 kgms. per sq. cm., depends on the presence in the colloidal state of the substances mentioned; these cause this quite considerable force uniting concrete and iron. In the different ferro-concrete systems, Monier, Hyatt, and others attempted to bring this adhesion to the highest possible value by embedding iron rods and wires in various ways. In consequence of the strong adhesion, iron with external unevenness is not necessary.

Lime
Mortar.

In ordinary lime mortar also these colloidal hydroxides play the same part; small admixtures of clayey and muddy components may be contained in the sand added, which increase its capacity for hardening.

¹ Cf. P. Rohland, Betonztg. 3, 49 (1909).

There was another problem in the industry of clay, Clay and which was capable of solution by the help of substances in the colloidal state.

Porcelain
Manufacture.

Different solutions were brought forward on the question of the cause of plasticity, but none were found sufficient; a point was first reached by colloidal investigation at which the door was opened to a region hitherto little known scientifically.

The previous suppositions on the causes of the plasticity of clay were based on various properties which were attributed to clay particles; porous mesh-like structure, spherical form, pliancy without elasticity, complete power of cleaving, flexibility, small spherical form, smooth surfaces, condition full of pores (tending to matting), power of displacement, rough surfaces, and others. Other authors sought for the causes of plasticity in the "arrangement of the single molecules and atoms" in the sense of the organic structural hypothesis, or in conceptions borrowed from physical teaching, such as adhesion and cohesion, which are only mere "conceptions" inaccessible to scientific treatment, and thus came to no result. All these statements have this in common—that they do not go beyond more or less good comparisons; they do not show the particular causes of plasticity.

For example, a spherical form with smooth surfaces can be assumed in sand free from clay; however, this never gives a plastic mass.

The real explanation for the causes of plasticity must be this: that clay in the air-dried state contains substances in the colloidal state and forms them in contact with water (the already-mentioned hydroxides of silicon, aluminium and iron, and probably organic substances), and further, that these substances in the colloidal state possess plastic properties; colloidal nature and plasticity stand in causative connection.

Thus clay slate when freshly broken is a completely unplastic material; it first possesses plastic properties after it has "decomposed" for a long time, when in contact with water it forms the above-named substances

in the colloidal state. That pure kaolin is very slightly plastic, indeed can be unplastic, is due to the fact that these colloidal hydroxides of silicon, aluminium and iron are first formed, and then carried away by the water in the kaolinisation of granitic rocks.

Clays containing zinc, which contain practically no aluminium silicate, are strongly plastic on this account, since in contact with water they form substances in the colloidal state, the hydroxides of zinc and silicon.

The clays have consequently the power of absorbing water, which is connected with the contraction in taking up water, and a maximum of swelling, capacity for shrinking on drying in air and in fire, power of binding small amorphous and crystalloidal substances, the so-called thinners; in the coagulated state they possess the property of hindering diffusion and arresting other colloidal solutions; while they allow solutions of crystalloidal substances to diffuse; finally, they have the capacity of adsorbing dyestuffs of complicated structure, and different kinds of ions, carbonic and boric acid ions completely, and phosphoric acid ions partially, further, unsaturated hydrocarbons of the composition C_nH_{2n-2} , C_nH_{2n} , and finally strong and even foetid odours.

Classification and Purification of Effluent Waters.

Since, therefore, these clays adsorb and retain substances in the colloidal state—such as oils, fats, concentrated soap solutions, starch, dextrin, maltose, glycerine, plant and animal albumin, casein, etc., further, inorganic dyes, such as Prussian blue and Turnbull's blue, all coal-tar dyes, colours, the colouring matter of beer, all plant colouring matters, indigo, curcuma, the colouring matter of the carrot, berberine, the colouring matters derived from various woods (Brazil wood, logwood, fustic), animal colouring matters, such as carmine, the colouring matter of the blood, the yellowish-brown colouring matter of urine, faecal matter, further, all bad odours, certain hydrocarbons and kinds of ions—they are suitable for clearing, decolourising, and purifying the effluent waters of factories and works, which contain many

substances in the colloidal state and many colouring matters, those of the carbohydrate industries, starch and dextrin, dyeing, tanning, soap-boiling, paper and sugar works, breweries and distilleries, and finally town sewage.¹

It is exactly these effluents, containing many substances in the colloidal state and many colouring matters, which can be purified only with difficulty, or indeed, not at all, by other previous methods—mechanical separation, the addition of chemicals, irrigation and the biological method, and the electro-chemical method.

On the other hand, it is these substances especially which, when they pass from the effluents into slowly flowing waters in particular, injure and destroy plant and animal life.

If the effluents contain no agriculturally injurious substances, the clays which have accomplished the adsorption can find application as manures, or they can be advantageously employed in the ceramic industry, since their degree of plasticity has been raised by addition of substances in the colloidal state.

On this basis also may be considered the means which find application for raising and diminishing the degree of plasticity.

The so-called decomposition of clay serves the former of Clay. purpose; this is performed in cool and moist cellars, and finds especial application in the manufacture of porcelain; thereby is brought about essentially an increase in the colloidally dissolved substances of the clay, already mixed with felspar, etc. After some time the mass of clay shows an alkaline reaction, derived from the hydrolytically decomposed felspar. Further, a decomposition then occurs of the organic substances present in the clay and in the water used; this is an acid fermentation which depends on physiological processes, perhaps the activity of bacteria, probably of

¹ Cf. P. Rohland, Die chemische Industrie, 33, 5 (1910). The method of purifying effluents and sewage by clay.

ferments. Thereby the alkalinity of the decomposing clay is arrested; hydrogen ions are produced which accelerate the coagulation of the substances in the colloidal state, whereby the degree of plasticity is raised.

For this purpose inorganic and organic colloids, aluminium hydroxide, silicon hydroxide, agglutinated starch, tannin, gluten, etc., are added before decomposition.

During decomposition the following process further takes place; in a mass of clay soaked with water a contraction occurs in consequence of the content of substances in the colloidal state; the volume of the swollen clay is smaller than the original volume plus that of the absorbed water. This contraction is accompanied with the evolution of heat.

By lowering of temperature, such as occurs in cool cellars, absorption of water and contraction proceed to a greater extent, which likewise results in raising the degree of plasticity.

Wintering and Summering. In ordinary clays, the raw material of pots, bricks, etc., as a rule, only "wintering" and "summering"¹ occur; the object and result is the same in both. In the first case the clay is piled up in long heaps 60 to 90 cm. high, frequently stirred up and watered; in the latter case it is spread on the ground in thin layers.

Thereby a mechanical loosening of the clay occurs; the chemical processes consist in the oxidation of substances poor in oxygen, ferrous to ferric salts, iron sulphide to ferrous sulphate; the most essential is that by the repeated moistening with water, the amount of colloids in the clay is increased, and thereby the degree of plasticity is raised.

The reverse process, the diminution of the degree of plasticity, is effected by addition of alkalies; the coagulation of the colloidal hydroxides is retarded or arrested by the hydroxyl ions of the alkali; salts which

¹ [Auswintern and Aussommern.]

contain hydroxyl ions in the solution by hydrolysis, *e.g.*, sodium and potassium carbonates, find application as well as alkalies; yet in these the influence of the hydroxyl ions may be weakened, compensated or even strengthened, by the kathodic element of the salt in question.

Only clays which contain quite definite organic substances permit such diminution of the degree of plasticity, or "fusion"; in a clay from the kingdom of Saxony these are of a fatty nature and are hydrolysed by addition of alkali; on such clays hydroxyl ions exert an action partly liquefying, partly coagulating; the latter influence is exerted on these soapy substances, as will be shown later in soap manufacture.

This "fusion" of the clay by alkali finds technical application in the manufacture of pottery and enamelled ware; this process is particularly valuable, and especially for the latter, since when it is manufactured in another way it shows a smaller degree of resistibility.

As already mentioned, the action of alkalies or hydroxyl ions on clays, which finds expression in a diminution of the degree of plasticity and a "fusion" is based in general on a mutual repulsion, according to electrostatic laws, of the colloidal particles charged with negative electricity, and the hydroxyl ions; the action of acids or hydrogen ions, which accelerate coagulation, comes about because these, being charged with positive electricity, attract the negative colloidal particles, forming complex masses and thus bringing about coagulation.

Substances in the colloidal state play a not inconsiderable part in the manufacture of soap; concentrated soap solutions possess a marked colloidal character; they have the same tension and the same boiling-point as pure water, a very small elevation of the boiling-point and depression of the freezing-point, and small osmotic pressure.

Through these properties of soap solutions can be explained rules which have been empirically obtained

in soap manufacture.¹ Each soap undergoes the so-called "rectification"²; this signifies that not only the quantity of alkali stoichoimetrically necessary for saponification is added, but that a definite excess is necessary after saponification.

When a mixture of oils has been saponified with alkali by the first process only, a soft soap is formed of fluid nature; but by the excess of hydroxyl ions a coagulation of the colloidal soap solution occurs.

The coagulating action of the hydroxyl ions comes into play in soap manufacture in yet another place, and indeed, in a manner at first disadvantageous. To weaken or prevent it a carbonate, soda or potash, is added in the so-called "causticity reaction." This name comes from the time when the soap-boiler prepared his own lyes; he causticised soda and potash solutions by lime, and thus obtained lyes of a definite "lime ratio," *i.e.*, ratio of caustic to carbonate. If the content of the latter was too low he rendered the lye "lower in lime" or "reduced the causticity" by adding soda or potash. This process was called "grading."³

But if the addition of carbonates is increased during the "caustification reaction" the coagulating action of the hydroxyl ions comes into play, so that the soap is thick and viscous. The solution in the kettle consists of the alkali salts of the fatty acids formed during saponification, together with caustic alkalies, alkali carbonates, and other salts, and is of a colloidal nature.

This influence inhibiting the coagulating action is to be ascribed to the carbonate ions. These ions exert here a similar influence to that of the hydroxyl ions on clay. It consists in a sort of protective action, in that it hinders coagulation.

Such protective action is already known in other colloidal solutions. Colloidal gold or platinum is more stable in alkaline than in pure water; small quantities of

¹ P. Rohland, Chem. Ind. 30, 20, 1907. The action of Hydroxyl ions in soap manufacture.

² *Abrichtung*.

³ *Versetzung*.

hydrogen ions retard the precipitation of ferric hydroxide. Further, albumin and gelatine raise the stability of inorganic colloidal solutions, so that they cannot be precipitated out. In this way also is to be explained the protective action of the carbonate ions.

The extraction of sugar from beetroot could not be performed relatively so easily if the division of substances in it into the crystalloidal and colloidal states did not render this possible. It depends on the different properties of both in diffusion through a membrane.

After the division of the beetroot into shreds, which are extracted with water at a fairly high temperature, the walls of the single beet cells behave as semi-permeable membranes.

The process of separation is based on this semi-permeability of the walls of these plant cells, while the substances in the crystalloidal state, sugar, inorganic salts, etc., diffuse through the walls, the substances in the colloidal state, proteins, pectins, gum, are held back; or the former pass through the pores of these semi-permeable walls with great ease and speed, while the latter pass through quite slowly and only with difficulty. This diffusion first begins in the cells at the surface of the shreds, but continues from cell to cell, so that by sufficiently long action and with frequent renewal of the water the whole sugar content can be extracted.

The method of extracting the beet shreds electro-chemically depends also on the presence of colloidal substances, and their property of wandering to the anode in the direction of the negative current.

Though the art of dyeing fibres, linen, wool, silk, is Dyeing so old, the theory of dyeing is of quite recent date. There are dyes which combine with plant and animal fibres without further treatment, while in others this is only accomplished after mordanting with an organic or inorganic substance.

Presumably the theories of dyeing will offer explanation to a still greater extent, when the knowledge of the adsorption of dyes by substances in the colloidal state,

and of adsorption phenomena in general, is yet further advanced.

Textile fibres possess a colloidal character; in the moist and swollen state, which they assume by treatment with acids or alkalies, they easily absorb other substances, *e.g.*, dyes. Dyeing must be considered as an adsorption process.

This explains the necessity, well known from a technical point of view, that in wool printing the atmosphere and the wool itself must possess a certain degree of humidity, so that the colour may completely develop and be retained; the cause of this is to be found in the fact that the moist wool swells in water vapour and passes into the colloidal state, and then adsorbs the dye.

A further proof of the colloidal nature of textile fibres is this: the adsorption of the dye is accelerated by the acidification of the bath in which the wool is dyed, but it ceases on subsequent dyeing in a bath without acid; this is because the wool again passes into the normal condition when it is no longer in contact with the acid bath.

Also fibres of the type of silk, *i.e.*, fibroin, show colloidal properties; a silk fibre can be loaded with foreign substances up to 250 per cent. without losing its appearance and lustre. This again is only rendered possible by substances in the colloidal state—*e.g.*, albumins; the stronger the colloidal nature of a substance, the greater is its power of adsorption.

The felting of wool and hair is brought about by the transformation of the fibre to the condition of a gel, by an alkaline or acid bath; adherence is caused by mechanical felting.

The fact that mercerised cotton will dye easier and darker than ordinary cotton can also be explained by its colloidal structure. By the action of soda lye the cotton passes into a gelatinised condition, which persists after repeated washing and favours the adsorption of the dye.¹

¹ Cf. E. Justin-Mueller, Zt. f. Ind. u. Chem. d. Koll. (The nature of textile fibres), I. 11, 1907.

Both animal and vegetable fibres, of the former, principally the albumins, of the latter, carbohydrates, are of colloidal nature. All these processes completely recall the adsorption of dyestuffs of complicated structure by clay and talc, also the insolubility in water caused in these dyestuffs by adsorption ; there is this in common, that they have their causes in the peculiar structure of substances in the colloidal state.

In the finishing of printed cotton materials substances in the colloidal state also find application ; they are finished to improve their outward appearance ; a substance in the colloidal state, such as starch or dextrin, is pressed into them.

The industry of tanning also requires substances in Tanning. the colloidal state ; animal hides were first rubbed with fat and thus made supple ; later the use of gall-nuts, oak bark and tan, pine bark, quebracho wood, etc., was learnt ; all these natural products contain colloidal substances, tannic acids, of which tannin, digallo-tannic acid, is the most accurately known. Animal and mineral tans also contain substances of a colloidal character, the degree of which is of essential significance.

The theory of tanning which best answers to facts, regards the processes, particularly in the swollen state of the hide, as processes of adsorption.

Our youngest industries, those of automobiles and airships, likewise require substances in the colloidal state—rubber, gutta-percha, and celluloid. Motors and Airships.

Rubber, the latex of tropical Euphorbiaceæ, becomes brittle and unelastic in the air by oxidation ; as such it serves for the manufacture of erasers, tubes, plates ; by heating with molten sulphur (10—15 per cent.) it is changed into the so-called vulcanised rubber, whereby it acquires an elasticity which remains on heating. Extensive researches have been recently made on this process.¹

By heating with a larger amount of sulphur to 120—

¹ Cf. R. Ditmar, Zt. für Chemie und Industrie der Kolloide, 1906—1909.

150° , rubber is changed into a horny modification which finds application in the manufacture of combs, pen-holders, etc., as ebonite or hard rubber.

Gutta-percha, likewise a dried-up tropical latex, is tough and only slightly elastic at ordinary temperatures, but at higher temperatures (60 — 70°) it can be easily shaped; it principally serves, as the second modification of rubber, for the manufacture of tubes, pneumatics, etc.; it is further employed in the manufacture of cables on account of its electrical insulating power.

Celluloid, a mixture of a colloidal substance, colloidion, with camphor, has found much application in the erection of the last Zeppelin airship.

The working of resins and the manufacture of varnish is essentially based on substances in the colloidal state.

Paper Manufacture. Both the older paper manufacture, which worked up rags, and the newer, which starts from cellulose, has frequently to deal with substances in the colloidal state; in "water sizing," a process in which the property of running is taken from the paper, a solution of resin in soda lye, starch, alum or aluminium sulphate is added. Resinic acid is thus precipitated, which remaining mixed with the paper prevents running, while the starch hinders the precipitation of the resinic acid on account of its colloidal condition.

Tungsten Lamp. In the manufacture of the tungsten lamp the metal tungsten in the colloidal state plays a characteristic part. This metal has indeed the advantage of possessing a high melting-point ($2,800^{\circ}$), but it is too brittle to be drawn out into wires; its colloidal solution is first formed by a suitable chemical treatment of the crystalloidal tungsten; it can then be precipitated in the colloidal state.

The metal in the colloidal state is no longer brittle, but can be easily drawn out into threads, so that it can be employed for the purpose of illumination.

Gold Ruby Glass. In the manufacture of gold ruby glass a colloidal solution of gold is employed; it is formed when gold chloride is added to glass; by sudden lowering of temperature a colourless glass first results. Gold in the

colloidal state is formed by repeated heating, in consequence of which the glass acquires a superb colour. These processes can be rendered visible with the aid of the ultra-microscope.

The long known gold purple of Cassius is also of a Purple of colloidal nature; it is obtained by reduction of a gold Cassius. hydrochloride solution with a solution of stannous chloride. A most remarkable phenomenon then occurs, a sort of mimicry between two substances in the colloidal inorganic state which is otherwise only found in organised nature between certain plants and animals. The colloidal solution of gold has completely assumed the properties of stannic acid hydrosol in chemical respects, while it has only communicated its colour to the latter.

In the manufacture of silver and gold mirrors colloidal Silver and solutions of gold and silver are of importance; in these Gold metallic silver is precipitated from a crystalloidal silver Mirrors. solution by a reducing agent; thereby is obtained transiently the red colour of a colloidal silver solution. It is now necessary to precipitate it from this colloidal solution, which is so sensitive to external influences, in such a form that a beautiful silver or gold mirror results. The condition of the glass surface is of importance here.

The activity of the dry cell depends on the electro-^{Dry Cell.} lytic conduction occurring in the coagulated gelatine to the same extent, and according to the same laws, as in water.

Mankind is indebted to matter in the colloidal state Blasting for Alfred Nobel's blasting gelatine. By combination of Gelatine. collodion or soluble gun-cotton with nitro-glycerine he obtained a mass of gelatinous or gum-like consistency. The proportion is about 93 per cent. nitro-glycerine and 7 per cent. soluble gun cotton; it is an amber yellow transparent elastic mass, which can be kept for a very long time under water. It explodes at 204° on slow heating, 240° on rapid heating.

Its great advantage over other explosives, such as dynamite, is that it is quite considerably less sensitive against shocks; blasting gelatine first explodes with a shock of $3\frac{1}{2}$ kgms., or it must be vigorously detonated.

This great resistance against shock, etc., which would not be possible with a crystalloidal body, is a consequence of the colloidal nature of the blasting gelatine.

Gun-cotton.

Further, it was first possible to prepare a smokeless powder by using a substance in the colloidal state, gun-cotton. Here the application of a substance in the colloidal state has brought about a change in the tactics and strategy of war, which can be considered of equal importance with the discovery of the first black gunpowder.

Photography.

A smaller technical advance is signified by the introduction of gelatine for the development of scientific and artistic photography; and an advance of great importance to civilisation has been made by the introduction of culture-gelatine for bacteriology.

An alchemist, Heinrich Schulze, made the first "photographic" observation in Halle-a.-S. in the year 1727; he dissolved silver, which stood in the sun, in nitric acid, and poured this solution on chalk; he then remarked to his astonishment that the side of the chalk turned to the sun was coloured dark, while the other side remained white.

Daguerre exposed a silver plate to the vapours of iodine, and allowed the image of a camera obscura to act upon it; after the action which followed, the plate was brought into the vapour of gently warmed mercury, whereby a picture was conjured forth.

But it was the application of a substance in the colloidal state, first collodion, then gelatine, which produced a great advance in photography.

Glass plates were covered with gelatine in which there was a layer of silver bromide sensitive to light; the plates thus prepared cannot be used at first, but must be stored; the plates, at first transparent, become opaque; the particles of silver bromide agglomerate, and then possess the maximum of sensitiveness to light.¹

¹ Considered at length in Dr. Lüppo-Cramer, "Kolloidchemie und Photographie." Th. Steinkopff, Dresden.

This property of the haloid silver salts presents many problems which can only be further elucidated by the study of colloidal chemical phenomena.

An external change of colour cannot be perceived on an illuminated silver bromide plate; it is first recognisable on subsequent development with a developer, when the parts of the silver bromide, more or less attacked by the radiant energy, react with correspondingly greater or smaller velocity.

Through this there first appears a visible change of the silver haloid; a blackening occurs, resulting from the metal and metal oxide compounds which separate.

All these processes are only possible in a colloidal medium; a characteristic adsorption phenomenon is here in question, and in combination with it stands the slowness of reaction of the silver bromide, which does not react directly to the radiant energy, but first manifests a greater reaction velocity through a developer.

It was a substance in the colloidal state whose application brought one of the greatest blessings to all mankind. Bacteria are themselves of colloidal nature; it was first possible to learn more intimately their conditions of life, when a foodstuff was found in which they could develop and be obtained in the greatest purity. The introduction of culture-gelatine, by Robert Koch, rendered possible the growth of pure cultures, and the discovery of methods to make uninjurious these small but extremely dangerous enemies of mankind.

The chemistry of foodstuffs has much to do with Chemistry of Food-stuffs. substances in the colloidal state; our foodstuffs come from plants and animals, which for the most part consist of colloids. Flesh, blood and brains are of colloidal nature; the manufacture of carbohydrates, starch and dextrin, is exclusively occupied with colloidal bodies. Potato starch, wheat starch and arrowroot are the principal representatives of this class.

The processes in the preparation of dough and in Baking, baking take place in colloidal media; the protoplasm of yeast cells is of colloidal nature; fermentation is a process which can occur, with its characteristic

absorption of water and swelling, only in substances in the colloidal state.

In baking, the starch is transformed into dextrose and caramel-like products; the proteins undergo partial changes, albumins are transformed into the coagulated state, casein and fibroin unite with the swollen particles of starch.

When unpalatable bread results in baking, the cause is to be sought in the processes of change of colloidal substances of the starch, the adhesive which influences the goodness and taste of the bread.

Brewing. Beer is essentially a solution of carbohydrates, *i.e.*, colloidal substances and the constituents of hops, which are partially electrolytes; the strong foam formation comes about by action of the free acid in the beer, *i.e.*, hydrogen ions on the colloids; in the process of brewing, starch and especially protein from the grains of malt are changed into a colloidal extract soluble in water. The colloids of beer, like those of clay, also adsorb carbon-dioxide.¹

The raw materials of pure beer, hops and malt, develop and change in brewing, under the action of the colloidal yeast protoplasm, into numerous substances in the colloidal state, hop oils and resins, starch, dextrin, maltoses and albumins.

Distilleries.

Brandy and potato spirit distilleries also partially utilise substances in the colloidal state, raw materials containing starch, grain and potatoes; the change into further colloidal substances, dextrose, maltose and iso-maltose is effected by a ferment, the diastase of malt.

In Italy, maize starch is treated with dilute sulphuric acid under 2—3 atmospheres pressure, and thereby, beside dextrin and iso-maltose, dextrose or grape sugar is formed; this is one of the rare processes in which a crystalloid substance is formed from substances in the colloidal state.

Dairies.

Cows' milk, the initial product in dairy work (utilisation of milk, obtaining cream, butter and cheese) is of

¹ Cf. Zt. Phys. Chem. 49, 3, 322.

colloidal nature in its most important constituents; besides the crystalloidal water, which can be present up to 90 per cent., inorganic salts and the crystalloidal milk sugar, the substances present in the colloidal state are proteins, especially casein, with some albumins and fats.

In butter-making the fats and the milk are utilised, while by coagulation of the casein by acids or by a ferment, by addition of rennet, curds are obtained, which are further worked up into cheese.

The elements of artificial butter or margarine also are largely substances in the colloidal state, animal fats and plant oils.

Finally, numerous industries, washing and ironing, book-binding, use substances in the colloidal state, especially carbohydrates, potato starch, wheat starch, etc.

Dextrin, which is obtained by heating starch, dry or treated with a small quantity of acid, is likewise applicable in many industries for finishing fabrics, glazing paper, etc.

This short glance over the regions of technology and Industry. industry should make the significance of substances in the colloidal state in this connection sufficiently clear; they appear to be almost more valuable for us and our civilisation, than those in the crystalloidal state; technology and practice have earlier recognised and utilised this value than chemical, physical and physiological science, which have only recently given their attention to the phenomena of matter in the colloidal state.

It is to be hoped now that light will fall from the most different sides on these phenomena, still enshrouded in darkness; at present a large number of investigators are occupied in this field; it is to be desired that through this work, and through a common activity of technology and science, significant usefulness and advantage will be experienced.



The significance in nature of substances in the col- Nature
loidal state has hitherto not received the attention and
Colloids.

Mines-
mology
and
Geology.

which it deserves. It is precisely here that mineralogists and geologists have turned their interest almost exclusively to bodies in the crystalloidal and amorphous states.

Yet the presence of colloidal substances could be easily recognised; they occur in many disintegrations, e.g., in those of granitic rocks or feldspars; in the formation of trass in the Netta and Brohl Valleys in the Rhine district, in the ries in Württemberg and in the Italian puzzuolane; the resulting colloidal substances are the hydroxides of silicon, aluminium and iron.

In a weathering reaction on a large scale in an earlier period of the earth's history silicic acid was likewise deposited, presumably mostly in the colloidal form. In consequence of lowering of temperature, the system previously in equilibrium, silicate and carbon-dioxide, was disturbed, so that this change must follow, and in the direction that carbon-dioxide was bound, carbonate was formed, while silicic acid separated. This reaction also occurs now, though with significantly smaller velocity, since the quantity of carbon-dioxide in the air is very much diminished. But at that time carbon-dioxide "corroded" granitic rocks.

Further, spathic iron ore undergoes a process of weathering, in which ferric hydroxide, a substance in the colloidal state, finally remains; the ferrous carbonate is decomposed by the action of water, when the hydrogen ions of the water and the carbonic acid ions combine to form undissociated carbonic acid, and ferrous oxide remains, which is then further transformed to ferric oxide and hydroxide. The zeolites, hydrated sodium aluminium silicates, also furnish substances in the colloidal state on weathering, the hydroxides of aluminium and silicon.

Petrifica-
tions.

Further, probably these and other substances in the colloidal state, e.g., calcium carbonate, have given rise to petrifications in this form.

Weighty examples of substances in the gel state in nature are bauxite, the opal with its coloured varieties, psilomelane, brown iron ore and others; not only single

minerals, but also mixtures of gels occur in the coagulated state. The opal also occurs in nature in the gelatinous state, likewise arsenical iron ore.

The formation of mud depends on the action of very finely divided small particles, with the aid of substances in the colloidal state, essentially the hydroxides of silicon, aluminium and iron, with organic colloids resulting from plant and animal remains.

Firstly, all the substances in the colloidal state are precipitated and deposited at suitable places. The plasticity of river or sea mud is due to these substances; and it was this property which caused men in the earliest stages of their culture to apply it in the manufacture of vessels, and later to dry and burn them.

By the above described formation of deltas the present mud deposits at the mouth of smaller and larger rivers are to be explained.

Colloidal substances, and indeed, again, the hydroxides of silicon, aluminium and iron, and those of an organic nature, have a much greater value from the point of view of agricultural chemistry and plant physiology than has been hitherto assumed.¹

They have arisen in the decomposition of granitic rocks, of felspars. These double silicates undergo hydrolysis and suffer the action of elements of the atmosphere, carbon-dioxide of the air and moisture, also the action of acids in soil, which break up the living plant roots and decaying plants and form from them humus substances and humic acids; in these processes colloidal silicon hydroxide, aluminium hydroxide, and iron hydroxide are formed, while the alkali which is simultaneously split off is transformed into carbonate.

Starting from a felspar, orthoclase, which in its purest form possesses the composition of a double silicate, the process of decomposition which leads to

¹ Cf. P. Rohland, *Landwirtschaftliche Jahrbücher*, 473 (1907), 273 (1909), 369 (1910).

substances in the colloidal state depends on the solution of the soluble alkali silicate by water, and by its hydrolysing action the hydroxides of silicon and aluminium are separated in a colloidal form.

But if these substances in the colloidal state are continually washed by water, pure aluminium silicate (kaolin) frequently remains, which is no longer decomposed by water, or at least only slightly so; thus kaolin answers in composition to the chemical formula $2\text{SiO}_2, \text{Al}_2\text{O}_3, 2\text{H}_2\text{O}$, which is valueless from an agricultural chemical point of view, but is of high technical significance.

Soils containing clay are accordingly those which form these substances in the colloidal state in contact with water; these determine the slipperiness of the soil, they increase the firmness of the roots of many plants, and are determinative for the capacity of absorbing water and for permeability.¹

The more the soil contains such colloidal substances, the more of these which are present in a deposited and coagulated state, the greater is the degree of its impermeability to water; the smaller the clay content, the less marked is the capacity of taking up water; the most permeable soil is that free from clay and rich in sand.

The view expressed by E. Wollny² and given in the text-book of A. Meyer,³ "that one and the same clayey soil will be more impermeable, the closer its particles touch one another, and that the impermeability can be expressed as a resistance to filtration increased infinitely in consequence of the surfaces closely touching and rubbing against one another," can be designated as superficial and erroneous; it does not touch the true cause of impermeability, for soils whose particles are closely compressed can nevertheless be permeable, i.e., compressed quartz!

¹ Cf. P. Rohland, Zt. "Aus der Natur." Colloidal substances in Nature.

² Forschungen auf dem Gebiete der Agrikulturphysik, 1891.

³ Agrikulturchemie, 1902, Bd. II. 1, Abt.

The degree of water absorption depends on the temperature: the absorption of water following on swelling depends on a phenomenon of contraction, which is connected with evolution of heat. According to the Maupertuis-van't Hoff law (which states that "on cooling, processes take place proceeding with the evolution of heat, while on warming, reactions follow which cause a cooling"; if cooling sets in, processes occur which involve heat, *i.e.*, greater absorption of water, while on rise of temperature the capacity of absorbing water is diminished, and on more vigorous warming shrinking occurs.

Sunbeams, rain and wind, and the colloidal substances of soil stand in the most intimate relationships.

Soils containing clay are semi-permeable in consequence of their content in colloidal substances; they permit the passage of crystalloidal dissolved substances, such as sodium chloride, sulphates, etc., with quite few exceptions, but not those which are colloidally dissolved.

These facts are of great significance for the growth of plants; for all food salts are of crystalloidal nature as far as is known at present, with one exception, so that they diffuse without hindrance through the colloidal layers of the soil. The one exception is that tobacco plants use an alkali silicate as a cultural liquid, *i.e.*, a substance in the colloidal state.

The colloidal substances in soils containing clay have Manuring. finally the power of adsorbing and retaining certain kinds of substances; soils containing clay adsorb dye-stuffs of complicated constitution, the dyestuffs and also the colloidal constituents of urine and faecal matter, and therefore essentially influence manuring.

The cause of this adsorption is to be sought in the structure of the substances in the colloidal state, which is to be considered as a mesh structure, a continuous porous framework.

Hence Meyer's explanation¹ "that clays exert

¹ Agrikulturchemie, Bd. II. Abt. 1.

adsorption since they possess no definite capacity of saturation for bases on account of the double nature of alumina" does not appear sufficient.

Soils containing clay only adsorb $\text{CO}_3^{''}$ and HCO_3' ions from carbonates, $\text{B}_4\text{O}_7^{''}$ completely from borates, and PO_4''' ions partially from phosphates, as far as, and indeed in proportion as, they are able to form colloidal substances in contact with water.

It is worthy of note that, according to recent observations, boric acid ions act as "catalytic manures"; applied in the form of boric acid they cause a marked increase in the dry weight of plants.

In the last processes an exchange of the kathodic elements occurs mutually; according to the law of equivalence the calcium and sodium in the silicates can be substituted by magnesium and potassium. The significance of these substitutions, especially the replacement of sodium by potassium, from a plant-physiological point of view is made clear in the most significant way, because the potassium salts are much more valuable for the culture of plants than the sodium salts, and the latter are completely unnecessary for a whole number of growths, while potassium salts cannot be dispensed with. Perhaps the above described adsorption is only a phenomenon accompanying this exchange.

These processes are also of high significance for the question of lime and magnesia manuring, since the ratio between lime and magnesia must be considered in manuring, because too great a quantity of magnesia diminishes the highest yield, as too strong lime manuring acts injuriously.

The colloidal substances in soils containing clay also influence the solubility of the salts contained in them. This point is of significance in manuring with gypsum.

Manurial experiments with gypsum, which have remained without result, since, in consequence of the condition of the soil, the amount of the calcium salts

necessary for the physiological activity of the plant world could not be added, should largely be explained by a lack of consideration of this point.

When swampy soils completely adsorb PO_4''' ions, Swampy this process depends on the presence of substances in Soils. the colloidal state, which are formed by decaying plants.

The velocity of adsorption for all these substances can be catalytically accelerated by the presence of others; thus the oxidation, by absorption of oxygen from the air, of ferrous salts contained in arable soils, is energetically accelerated in presence of water or water vapour.

Finally, these substances in the colloidal state hinder Efflorescence. the efflorescence and deposition of salts soluble in water. In consequence of their structure, which is to be considered a mesh system, narrow-celled and widely branched, they can retain water and salts dissolved therein longer than amorphous and crystalloidal bodies can do so.

Dissolved salts wander inwards with the moisture from the surface of arable soil, and the layers next below, into the deeper lying layers where they can still be reached by the deeper roots of the plants.

The position is quite otherwise when the soil is practically free from substances in the colloidal state, when it is formed of sterile material, amorphous and crystalloidal substances only, sand, etc., on account of its small depth and complete drying. This is the case, for example, in many parts of Egypt, and in Namaland in German West Africa.

Then the soluble salts are not carried deep down, but rise to the surface with the water which evaporates, and crystallise out. In Namaland these efflorescences consist of magnesium sulphate, soda, Glauber's salt and other alkali salts, and in certain parts of Egypt these deposits were earlier so extensive, on account of the very rapid evaporation of water, that they could be used for obtaining soda.

Necessary as are these water soluble salts for the

culture of plants, they would be quite valueless from a physiological point of view if substances in the colloidal state were not simultaneously present with them in arable soil, which hinder them from efflorescing; without these our fields would wear shimmering white, instead of green garments, which would be caused by these deposits.

On the waste declivities which surround the manufactories at Stassfurt, which, free from colloidal substances consist largely of amorphous substances, by the action of dry and hot air white efflorescences of soluble salts appear, shining like freshly fallen snow, only to disappear again with the next rain.

If now all these processes, the formation of substances in the colloidal state, their coagulation and eventual solution, adsorption, do not proceed in arable soil with the exactness and completeness with which experiments take place in the laboratory, yet they occur in the same sense and in the same direction in greater or smaller velocity, sometimes accelerated, sometimes retarded by other influences, such as temperature change, solar radiation, etc.

Zoology. The significance of substances in the colloidal state is not yet exhausted; interesting relationships are shown from a zoological point of view.

Manifestly worms can move better in moist soils containing colloids than in amorphous and crystalloidal soils; but by their activity they contribute to the loosening of the soil and to its greater fruitfulness.¹

But also soils rich in colloids afford a more certain existence than sterile ones to other members of the small animal world, on account of their capacity of absorbing soluble salts and retaining them longer.

Summarising: Colloidal substances determine the degree of permeability for water, they have the property of semi-permeability, they permit the diffusion of the colloidal food salts of plants, they retain the colloidal

¹ Darwin, "The formation of vegetable mould by the activity of worms."

substances and colouring matters of urine and faecal matter, they enrich the soil with carbonic acid and phosphoric acid ions by adsorption, they thereby simultaneously render possible the exchange of the alkaline earths in silicates with the alkalies in solution, they influence the solubility of salts contained in and added to arable soil, and with all these processes they determine manuring; thus the conclusion is established that **soils containing colloids are the most fruitful!**

In the formation of wood a colloidal chemical process can be recognised, principally taking place in two stages, with which some crystalloidal chemical reactions are still connected.¹

Cellulose is first formed in the youngest plant structures as a chemically indifferent surface- or framework-body, which in the tissue and fibrous structures possesses a very great surface.

A thickening and wood-formation of this surface-body then occurs by adsorption and skin-formation from the colloidal procambial bodies of the cambial fluid.

Connected with this there are chemical effects and reactions in the "swollen," perhaps partially hydrolysed, adsorbrates; ester-formation and other condensations are examples.

Thus, according to the assumptions of general and selective adsorption and gel formation, lignin is a variable mixture of colloids deposited from the juices, especially the cambial fluid, of which part is reversibly, another part irreversibly, linked with the cellulose; a chemical combination is probable only as a subsidiary effect. This is the rôle of the important wood-forming sap.

* * * * *

At a certain period of the earth's history, which probably followed that in which, according to the

¹ Cf. H. Wislicenus, Zt. f. Chem. u. Ind. der Koll. 6, 1, 1910. Colloidal chemical processes in the formation of wood, and the material nature of wood and lignin.

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cosmological gas theory of Kant-Lamarck, all elements were present as such in the gaseous state of aggregation, presumably matter occurred frequently in the colloidal state; since this is simultaneously connected with much smaller reaction-capacity than is the case with crystalloidal substances, the periods of change would be of much longer duration.¹

Liquid Crystals.

There are certain cases of substances hitherto only known in the crystalline form, to the present about thirty, in which it has been found possible to bring about for long periods and to observe a state identical with the colloidal, before they are transformed into the stable crystalline form; they show the essential distinctions of such a state. These are the so-called liquid crystals, silver iodide above 146°, ammonium oleate, cholestryl benzoate, p.-azoxy-phenetol, p.-azoxy-cinnamic ethyl ester, azoxy-brom-cinnamic ester, p.-anisol-p.-anisidine, cholestryl caprate, p.-anisol-p.-amido-acetophenone, etc.

According to O. Lehmann² these complicated organic compounds, at temperatures which approach the melting-point, especially on addition of solvents, show a gelatinous softening of the microscopic particles with a rounding of the edges, and, finally, a liquefaction assuming the drop form.

It is noteworthy that there are some properties common to crystals in this state and to colloids themselves.

It is substances in the colloidal state which, in opposition to crystalloids, show a smaller or greater capacity for plasticity.³

But a certain degree of plasticity has been observed in the so-called liquid crystals.⁴

Further, substances in the colloidal state, such as the hydroxides of silicon, aluminium and iron, can

¹ Cf. P. Rohland, Zt. f. Chem. u. Ind. d. Koll. 1, 7 (1907).

² Annal. d. Physik. 728, 1905; 22, 1906.

³ Cf. P. Rohland, Zt. anorg. Chem. 31, 158, 1902. The plasticity of clay. *Ibid.*, 41, 325, 1904. The decomposition of clay.

⁴ Physikal. Zt. 7, 21, 1906.

absorb small amorphous or crystalloidal substances, as clays which form these colloidal substances in contact with water,¹ can absorb the so-called thinners.

This capacity of absorbing foreign substances has also been observed in the so-called liquid crystals.

The characteristic property of colloidal substances is, however, their great power of adsorption for dyestuffs.²

This phenomenon has also been observed by O. Lehmann³ in liquid crystals. Liquid crystals cover themselves with a yellow layer which is far darker in colour than the solution itself, just as if the liquid crystals attract the dyestuff to themselves from the solution with considerable force by adsorption and fix it on their surfaces.

A state has accordingly been observed in some groups of crystals for long periods, which presumably all crystallising bodies undergo, only with the difference that this state, lasting for a very short time, cannot usually be observed even with the most powerful microscope; the crystalloidal state is preceded by a condition in which the smallest particles, like those of substances in the colloidal state, are finely suspended in the solution; the crystal is then built up on these.

So "the two different worlds" of substances in the colloidal and crystalloidal state, as Graham designated them, are under certain conditions of identical nature.

From these observations and conclusions the following noteworthy analogy can be drawn: the evolution, through which the single individual substance now passes very rapidly in its formation each time, and which leads from the colloidal to the amorphous or crystalloidal state, in an earlier period of the earth's history, has led to the formation of that portion of Matter in the amorphous or crystalloidal form, though at a much slower speed.

The rapidly completed origination of a crystal

¹ Cf. P. Rohland, "Die Tone." Publisher : A. Hartleben, Vienna, 1909.

² Cf. P. Rohland, *ibid.*

³ Physikal. Zt. 11, 45, 1910.

individual is to be considered as a recapitulation of the slower proceeding formation of this class of Matter.

Biogenetic Law. This peculiarity recalls the principle which is designated as the biogenetic law of ontogeny and phylogeny; according to it the embryo undergoes the same evolution, but at a more rapid velocity, which has been manifested during long periods by the evolution of the human race.

Thus in inorganic and organic nature there is a process which runs parallel with one in organised nature.

It is not an unwarrantable assumption that since almost every substance under suitable conditions, and with appropriate methods, can be transformed into the colloidal state, the primary stage in the essential parts of the earth's history was not the crystalloidal, but the colloidal; the secondary is the amorphous and crystalloidal, which latter forms the summit in the formal development of matter. The colloidal, the amorphous, the crystalloidal state of matter signifies a rise in the form, but materially the colloidal stands far higher.

Physiology. In it occur, for the most part, plants and animals; in consequence of its cell and honeycomb structure it can be represented as the transition stage between inorganic, organic and organised nature; inorganic substances have already been prepared, which are similar to the proteins.¹

The colloidal state is generally characteristic for physiological processes, *e.g.*, for those in protoplasm, while substances in the crystalloidal state only possess subsidiary significance; protoplasm represents a colloidal and crystalloidal solution of complicated structure which, by addition and concentration change of electrolytes, suffers changes in constitution. For such processes, however, the above described slowness and incapacity of reaction of crystalloidal substances, which have been absorbed by those in the colloidal state, is of great importance; reactions can here fail which

otherwise occur between substances in the crystalloidal state, while others perhaps take place which cannot be realised under ordinary conditions.

Thus perhaps the account of the rhodian genius, Alexander von Humboldt,¹ may be taken in another sense.

As soon as the earthward turned torch of genius smoulders out, the butterfly flies upwards, the head of the genius sinks, young men and maidens gladly stretch out their hands, to follow their social instincts.

Without poetic language this means: As soon as what is called "Life" has vanished from matter in the colloidal state, the normal reactions again set in, which are known between substances in the crystalloidal state.

The widest outlooks for the most different branches Medicine, of medicine—therapy, pathology, balneology—open out in this field.

Thus, for example, the salts in urine acquire an increased solubility partially through colloidal admixtures, and these colloidal substances have an essential influence on the origination of sediment or on the formation of urinary calculi.

Now the effect exerted by the urine colloid on the solubility of the salts depends on the prevailing degree of stability of the colloid; it remains to be examined whether, and to what degree, the beneficial action of certain mineral waters in calculous diseases is connected with the change in the urinary solubility by colloidal influence. It also remains to investigate, in what way and to what extent, a balneological therapy can influence the growth of urinary calculi, that is to say, the combined growth of colloidal and crystalloidal urinary substances.²

It is also worth considering in what way electrolytes or ions influence the thickening or liquefying of the products of separation in the intestine, which are likewise of colloidal nature. Analogous processes are not

¹ "Ansichten der Natur." Bd. I.

² Cf. Zt. f. Chem. u. Ind. der Koll., 5, 1, 1909.

excluded here in which, like those occurring in clays, definite kinds of ions would cause coagulation and thickening, while others, again, would hinder this, and thus cause liquefaction; therapeutic means might then be taken on these lines.

The liquefying action of the $\text{SO}_4^{''}$ ions in magnesium and sodium sulphates should be ascribed to the property of these salts of attracting water.

Animal spermatozoa and ova, which possess the most important life functions, occur in the colloidal state; only in it, not in the crystalloidal, is possible that mutual power of permeation which is so wonderful in the reproductive processes.

The transference of the properties of the male and female individual to the embryo only appears possible and imaginable when it takes place in this peculiar finely divided colloidal state of matter. Whether spermatozoa and ova in the colloidal state are here considered almost microscopically small or as large as a house is all one, objectively considered.

A parallel between the combination of the colloids of animal ova and the individual inorganic and organic substances in the colloidal state is found in the following: the transformation of such a colloid, *i.e.*, a metal sulphide sol or a casein solution, into the coagulated state can be caused by addition of electrolyte.

But recent observations have shown that the development of animal ova, *e.g.*, of sea urchins, can be "artificially" caused by addition of an electrolyte (artificial parthogenesis).

* * * * *

"Mother of the Æneads, thou womb of men and gods, Venus, O thou, who pourest down cheerful brightness under the moving lights on heaven, on the navigated sea and the fruit-bearing earth; for all living existence is generated by thee to gaze on the rays of the sun . . . For thou alone rulest the Nature of Things; without thee nothing comes forth from the divine gate of light"—

—thus Lucretius Carus begins his poem on “The Nature of Things.”

Our observations and considerations on the colloidal and crystalloidal states of matter lead to another supposition about the “generation of living matter.”

If on our planet the transformation from inorganic-organic to organised, from lifeless to living, has principally occurred in the smallest shapes of the naked protoplasm, presumably this first state of birth was in the colloidal medium.

Organic colloidal compounds serve as the foundation for the formation of the first simplest organised forms; their structural parts, the different albumins, caseins, carbohydrates, only occur in nature in the colloidal state.

We are not only dealing here with the arrangement of the atoms and molecules and with the origination of certain movements, as represented by du Bois-Raymond,¹ but we must especially consider that the state, in which the single inorganic and organic compounds occurred, was of the greatest significance for the origin of life; this state was the colloidal.

We must also add that very probably catalytic phenomena should be considered in this connection. For positive catalysts are invariably active, as observation now shows, where the most remarkable phenomena take place, which are still shrouded in obscurity; ferments and enzymes, on the other hand, which are also of colloidal nature, are known in physiological processes precisely as positive catalysts.

Probably the picture which has been sketched of spontaneous or equivocal generation is erroneous in its essential parts, as it does not correspond to the actual phenomena which once occurred. Thus the distinction between autogeny, the formation of a simplest organised individual from an inorganic mother-liquid or from inorganic substances, and plasmogeny, the formation of an organism from an organic mother-liquid or organic matter already formed from inorganic substances, may draw us from the right path.

¹ Die sieben Welträtsel, 1880.

This is much more likely to lead to the colloidal state of matter, in which both inorganic and organic substances are united.

The conception must now be altered, in that from a complex of inorganic or organic substance, one has resulted, a naked cell or a monad.

It is much more likely that, from the colloidal state of the combined inorganic and organic matter, an intermediate product was evolved under suitable conditions, which was yet partially inorganic-organic, partially already organised.

Struggle for Existence. But this intermediate stage has perished in the "struggle for existence," since its conditions of life were extremely unfavourable; the now existing permanent forms, the simplest organisms, such as the monad, have developed from it.

It is noteworthy that Wöhler's urea synthesis (1828), on which too great hopes were once based with reference to the solution of the problem of life, was limited to a substance in the crystalloidal state, not to one of the substances in the colloidal state, so important for the phenomena of life. In consequence of this the hopes based on this synthesis have not been fulfilled.

Even if matter in the colloidal state, such as protein, could be artificially prepared synthetically, which might come about according to E. Fischer's experiments and results, a further distance would have to be traversed for the beginning of a scientific chemistry; at present far greater advances must be made; but substances in the colloidal state must form the starting-point for the formation of life.

The following point must be considered in this connection: possibly the first combination of inorganic and organic substances in the colloidal state to an organised body occurs between particles of matter, which in consequence of their enormous minuteness cannot be made visible even with our best auxiliary, the ultra-microscope.

This view cannot be discarded at once, since we know similar phenomena. There are important small particles of matter, which are perceived by our senses exclusively

by their smell ; they cannot be weighed with the finest analytical balances, even those which have been recently constructed, nor can they be made visible by any optical means. Yet the existence of such smallest particles cannot be doubted.

What will be later visible with the aid of the microscope is again reflected in the process of generation in a later stage, in which a naked protoplasm, a monad, finally a cell has resulted from the inorganic-organic-organised intermediate product in the colloidal state.

These suppositions are not new, they have been suggested in antiquity in quite a crude form ; they appear here, however, in a much more precise manner.

The old Greek natural philosophers held the view that the simpler forms of life originated from decaying hay, decaying dung, etc., therefore from colloidal media.

But these very facts could point earlier to a confirmation of these suppositions which was yet to come.

For it is an experience repeatedly confirmed, that in earlier periods of human history, great poets, prophets and philosophers have expressed presentiments, suppositions and approximations, to scientific theories, which were first recognised very much later as scientific discoveries of the first rank, or as natural laws, which have now first undergone exact experimental proof.

Greek
Natural
Philoso-
phy and
Modern
Natural
Science.

Thus the supposition of Heraclitus of Ephesus (500 b.c.), that the bodies then considered as elements dissolve in a fiery universal ether, is changed into the disaggregation theory of Rutherford and Soddy, according to which the atoms spontaneously decompose in stages and are transformed into electrons, the bearers of the luminiferous ether.

The supposition of Empedocles of Agrigent (460 b.c.), according to which first plants, then the animals, resulted by generation, but not in their present apparently suitable and harmonious forms, for in the struggle with the forces of nature those remained victors which were most advantageously formed, and therefore most capable of life, is similar to the evolution theory of Lamarck and Darwin, in which these suppositions are expressed

Monistic
and
Dualistic
Concep-
tion of the
Universe.

in a more precise form, their more intimate causes are discovered, and experimental proofs are advanced.

But this spontaneous generation, which appears so closely bound up with the colloidal state of matter, is the boundary-stone between the dualistic and monistic conception of the universe; neither the materialistic view nor energetics can succeed without being firmly based here.

Both materialism and energetics must recognise generation as unlimitedly necessary, at least unless they do not dispense with one solid foundation.

The dualistic view can dispense with generation, in that it starts out from the consideration that the Divine Omnipotence created matter in different states and different composition, inorganic, organic and organised matter; it can assume a particular act of creation for each new formation.

On the other hand, the dualistic view can bring the idea of generation and that of a creating Omnipotence in agreement by assuming a single act of creation of matter, in which already the germ of its future development was so implanted that from it inorganic, organic and organised nature could henceforth develop by stages in different states till they reached fruition in the origination of the first life.

"The fearful bell rings, and penetrates the blackened walls; the uncertainty of earnest expectation can endure no longer, the darkness already grows light; already it glows like living fire in the innermost phial, and a clear bright light, like a superb carbuncle, throws a flash through the darkness."

But even he who is most skilled in the reading of the future cannot say to what extent the monistic or dualistic conception should be embraced—even if a second "Wagner" succeeded in "composing" organised living matter "by mixing many hundreds of substances"—whether the atoms were previously "animated" apart from inorganic matter, or whether, and how, the increased energies, which we call Life, arose in dead matter.

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